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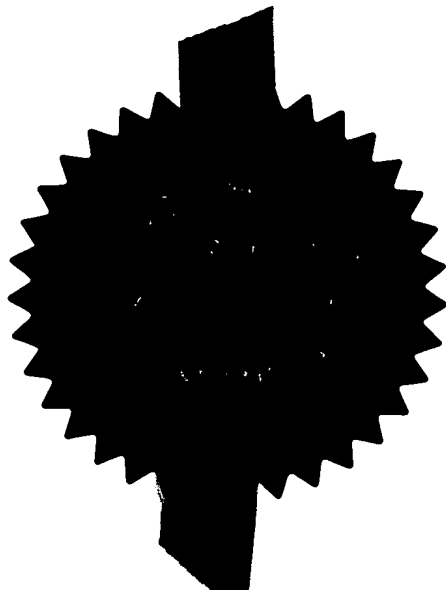
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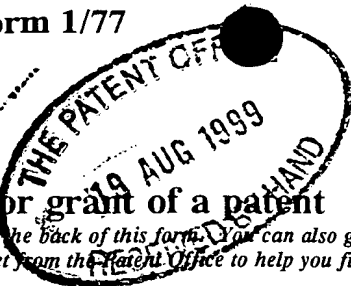
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2.	Patent application number (The Patent Office will fill in this part)	<b>9919718.8</b>		
3.	Full name, address and postcode of the or of each applicant (underline all surnames)	Borealis A/S Lyngby Hovedgade 96 DK-2800 Lyngby Denmark		
	Patents ADP number (if you know it)	06951438001		
	If the applicant is a corporate body, give country/state of incorporation	Denmark		
4.	Title of the invention	Process		
5.	Name of your agent (if you have one)	Frank B. Dehn & Co.		
	"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	179 Queen Victoria Street London EC4V 4EL		
	Patents ADP number (if you know it)	166001		
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)	
8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))	Yes		

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Description	11 ✓ <i>824</i>
Claim(s)	1 ✓
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Statement of inventorship and right to grant of a patent ( <i>Patents Form 7/77</i> )	-
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Request for substantive examination ( <i>Patents Form 10/77</i> )	-
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11. I/We request the grant of a patent on the basis of this application.

Signature *[Signature]* Date 19th August 1999  
Frank B Dehn & Co

12. Name and daytime telephone number of person to contact in the United Kingdom

Julian Cockbain  
0171 206 0600

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Process

This invention relates to improvements in and relating to the production of containers by blow moulding of a polymer material, in particular a high density polyethylene (HDPE).

In the production of containers using polymer materials, a variety of moulding techniques may be used, in particular blow moulding, slush moulding, injection moulding and rotational moulding. For very large containers, e.g. for use as oil or water tanks, rotational moulding is a preferred technique; however for medium to large sized containers, e.g. 8 to 250L volume, blow moulding is commonly used.

Generally in the blow moulding of containers a heated parison or extrudate is expanded to contact the interior surface of a mould by the action of pressurized gas within the parison and/or by application of a partial vacuum within the mould, e.g. by use of a mould having within its surface gas outlet vents through which a partial vacuum may be applied.

For blow moulding to be successful, the heated polymer must be able to stretch smoothly to produce a satisfactorily uniform skin in contact with the mould surface.

In the production of containers by blow moulding of polyethylene, the polymer used has typically been a high molecular weight (HMW) high density polyethylene (HDPE), generally with a melt flow rate (MFR<sub>21</sub>) in the range 2 to 12 g/10 min. Such materials may be produced for example by chromium-catalysed ethylene polymerization. However the choice of such materials essentially represents a compromise between the properties of the polymer, in particular the processability properties required for the blow moulding to be performed efficiently and successfully and the mechanical and chemical properties

required for the end uses of the blow moulded containers, e.g. impact resistance, stiffness, and environmental stress crack resistance (ESCR).

We have now found that large volume blow moulded containers which have excellent ESCR properties may be produced if one uses a high density polyethylene (HDPE) comprising at least two polyethylene components having different molecular weight distributions wherein at least one of said components is an ethylene copolymer. Such HDPE is referred to hereinafter as bimodal.

Thus viewed from one aspect the invention provides a process for the preparation of a 2 to 250L, more preferably 8 to 230L, still more preferably 30 to 225L, volume polyethylene container which process comprises blow moulding a bimodal HDPE.

In the process of the invention, the parison is conveniently part-blown before the mould is closed, the mould is then closed and the blowing of the parison is completed.

By polyethylene is meant a polymer the majority by weight of which derives from ethylene monomer units. While the different polyethylene components of the bimodal HDPE may all be ethylene copolymers, and while an ethylene homopolymer may be one of the components, the polyethylene components cannot all be ethylene homopolymers. Where one component is an ethylene homopolymer, this is preferably the component with the lower weight average molecular weight ( $M_w$ ) and its  $M_w$  is preferably 5000 to 100000 D, more preferably 20000 to 40000 D. In the ethylene copolymer components, comonomer contributions, e.g. up to 20% by weight more preferably up to 10% by weight, may derive from other copolymerizable monomers, generally  $C_{3-20}$ , especially  $C_{3-10}$ , comonomers, particularly singly or multiply ethylenically unsaturated comonomers, in particular  $C_{3-10}$   $\alpha$ -olefins such as propene, but-1-ene, hex-1-ene, etc. (The term ethylene copolymer is used herein to relate to

a polyethylene deriving from ethylene and one or more such copolymerizable comonomers). Moreover, the polyethylene may contain minor, e.g up to 10% by weight, preferably up to 5% by weight of other polymers, e.g. other polyolefins in particular polypropylenes, as well as additives such as plasticizers, colours, fillers, radiation stabilizers, antioxidants, etc., generally in amounts up to 10% by weight, preferably up to 5% by weight.

By HDPE is meant a polyethylene having a density of 940 to 980 kg/m<sup>3</sup>, preferably 945 to 975 kg/m<sup>3</sup>, more preferably 945 to 960 kg/m<sup>3</sup>, and a crystallinity of 60 to 95%, preferably 70 to 90%.

The HDPE used according to the invention is a bimodal or multimodal polymer. By bimodal (or multimodal), it is generally meant that the polymer consists of at least two fractions (components), one of which has a relatively low molecular weight and a relatively high density and another of which has a relatively high molecular weight and a relatively low density. Typically the molecular weight distribution (MWD) of a polymer produced in a single polymerization stage using a single monomer mixture, a single polymerization catalyst and a single set of process conditions (ie. temperature, pressure etc.) will show a single maximum, the breadth of which will depend on catalyst choice, reactor choice, process conditions, etc, ie. such a polymer will be monomodal.

A bimodal or multimodal polyethylene may be produced by blending two or more monomodal polyethylenes having differently centred maxima in their MWDs. Alternatively and preferably the bimodal polyethylene may be produced by polymerization using conditions which create a bimodal or multimodal polymer product, e.g. using a catalyst system or mixture with two or more different catalytic sites, using two or more stage polymerisation process with different process conditions

in the different stages (e.g. different temperatures, pressures, polymerisation media, hydrogen partial pressures, etc). (See EP-A-778289)

Such a bimodal (or multimodal) HDPE may be produced relatively simply by a multistage ethylene polymerization, e.g. using a series of reactors, with comonomer addition in only the reactor(s) used for production of the higher/highest molecular weight component(s). Examples of bimodal PE production are given in EP-A-778289 and WO92/12182.

If an ethylene homopolymer component is produced by slurry polymerization involving use of recycled diluent, that diluent may contain small amounts of higher  $\alpha$ -olefins as contaminants. Likewise where an earlier polymerization stage has produced an ethylene copolymer component, small amounts of comonomer may be carried over to an ethylene homopolymerization stage. Accordingly, by ethylene homopolymer is meant herein a polymer containing at least 99.9% by weight of ethylene units. Likewise as in a multistage/multireactor polymerization using more than one catalyst system, the homopolymerization catalysts may be at least partially active during the copolymerization reaction, any copolymer component making up less than 5% by weight of the total polymer shall not be considered to be the lowest molecular weight component in an HDPE according to the invention.

The copolymer component(s) of the HDPE used according to the invention will generally contain at least 0.1% by weight, preferably at least 0.5% by weight of non-ethylene monomer units, e.g. 0.5 to 6% of such comonomer units.

The polymerization reactions used to produce the HDPE of the invention may involve conventional ethylene homopolymerization or copolymerization reactions, e.g. gas-phase, slurry phase, liquid phase polymerizations, using conventional reactors, e.g. loop reactors, gas



phase reactors, batch reactors etc. (see for example WO97/44371 and WO96/18662). The catalyst systems used may likewise be any conventional systems, e.g. chromium catalysts, Ziegler-Natta and metallocene or metallocene:aluminoxane catalysts, either homogeneous or more preferably heterogeneous catalysts, e.g. catalysts supported on inorganic or organic particulates, in particular on magnesium halides or inorganic oxides such as silica, alumina or silica-alumina. For the preparation of the high molecular weight component in particular it is especially desirable to use supported Ziegler-Natta catalysts as the molecular weight can then conveniently be controlled using hydrogen. It is also possible to use supported metallocene catalysts as it is particularly straightforward to select desired molecular weights by appropriate selection of particular metallocenes. The metallocenes used will typically be group IVa to VIa metals (in particular Zr or Hf) complexed by optionally substituted cyclopentadienyl groups, e.g. groups carrying pendant or fused substituents optionally linked together by bridging groups. Suitable metallocenes and aluminoxane cocatalysts are widely described in the literature, e.g. the patent publications of Borealis, Hoechst, Exxon, etc.

Typically however the HDPE will be prepared using multistage polymerization using a single catalyst system or a plurality of catalyst systems, e.g. two or more metallocenes, one or more metallocenes and one or more Ziegler-Natta catalysts, two or more chromium catalysts, one or more chromium catalysts and one or more Ziegler-Natta catalysts, etc.

The use of bimodal HDPE in the production of relatively large, ie. 2 to 250L, preferably 8 to 240L, more preferably 20 to 230L, and still more preferably 30 to 225L, containers results in surprisingly increased values for ESCR. Thus for example tests comparing

containers made using conventional monomodal HDPE with bimodal HDPE have shown an increase in ESCR  $F_{50}$  from 250 hours to over 1000 hours. (ESCR  $F_{50}$  is measured as the time taken for 50% of samples to be broken when bent and contained in a detergent solution. The test is a standard one categorised as ESCR, ASTM D-1693 condition B, 10% Igepal). Such  $F_{50}$  values for relatively large containers are particularly surprising in view of the relatively low  $F_{50}$  values (ca. 400 h) achieved for small (0.45L) containers using blow-moulding of bimodal HDPE in EP-A-778289.

The bimodal HDPE used in the process of the invention preferably has the following characteristics  
Density: 940 to 970, preferably 945 to 960 kg/m<sup>3</sup>;  
Weight Average Molecular Weight: 200000 to 450000, preferably 250000 to 350000 Dalton;  
Number Average Molecular Weight: 6000 to 20000, preferably 7000 to 18000 Dalton;  
MFR<sub>21</sub>: 2 to 12 g/10 min, preferably 3 to 8 g/10 min;  
Molecular Weight Distribution: 15 to 55, preferably 18 to 50;  
Tensile Modulus: at least 900 mPa;  
Comonomer Content: 0.5 to 10% wt, preferably 1 to 2 wt %. Bimodal HDPE having such characteristics may be prepared by the technique described in EP-B-517868 or by conventional use of Ziegler Natta, metallocene or chromium catalysts.

The polymer used according to the invention preferably contains a high molecular weight component (e.g. with a molecular weight tail of about 5000000 Daltons) to increase melt strength of the HDPE composition under elongational deformation. This can be achieved in one of several ways, e.g.

(i) produce the HDPE in a multistage polymerization in which reactor conditions are set such that a very high molecular weight component is produced in one stage, e.g. by performing one reaction stage in the

absence of chain terminating hydrogen, by selection of a catalyst system which produces a high molecular weight polyethylene, by use of polyenic comonomers (e.g. dienes) which produce long chain branching or otherwise promote production of a high molecular weight fraction; or

(ii) crosslinking of a polymer by timed addition of crosslinking agents in the extruder whereby to tailor-make a high molecular weight grade (i.e. to add a HMW "tail" to the polymer).

Viewed from a further aspect the invention provides a blow-moulded binded HDPE container having a volume of 2 to 250L (preferably 8 to 240L, etc), and an ESCR  $F_{50}$  of at least 500 hours, preferably at least 800 hours, more preferably 1000 hours, e.g. 1000 to 2000 hours.

The containers of the invention may be produced in conventional blow-moulding apparatus.

It will be appreciated therefore that the containers of the invention may be produced without loss of the impact strength or ESCR properties using faster than normal blowing rates, ie. with more efficient and economical usage of the blow moulding apparatus.

The containers of the invention may be used indoors or out of doors for storing gases, liquids or solids, especially liquids such as water, glues, solvent-based soaps, paints, varnishes, chemical solutions, oils and other liquid chemicals. The containers may be open (e.g. tanks, basins, etc) or may be closed, for example with lids or caps or inlet or outlet ducts.

The invention will now be described further with reference to the following non-limiting Examples.

## EXAMPLE 1

### Catalyst Preparation

8.6g (66.4 mmol) of 2-ethyl-1-hexanol was added slowly to 27.8g (33.2 mmol) of 19.9% butyl-octyl-magnesium. The temperature was kept below 35°C

3.7g (1.0 mmol/g carrier) of 20% EADC (ethyl aluminium dichloride) was added to 5.9g of Sylopol 5510 silica/MgCl<sub>2</sub> carrier and the mixture was stirred for 1 hour at 30°C. 5.7g (0.9 mmol/g carrier) of the 2-ethyl-1-hexanol/butyl-octyl-magnesium complex was added and the mixture was stirred for 5 hours at 45°C. 0.6g (0.55 mmol/g carrier) of TiCl<sub>4</sub> was added and the mixture was stirred for 5 hours at 45°C. The catalyst was dried at 45-80°C for 3 hours.

## EXAMPLE 2

### Bimodal HDPE Polymer Preparation

Ethylene, propane and hydrogen were introduced at 2.4 kg/hour, 25 kg/hour and 1 g/hour respectively into a 50 dm<sup>3</sup> slurry loop reactor operated at 85°C and 65 bar. The catalyst of Example 1 was introduced at a rate sufficient to produce polyethylene (PE) at about 1.9 kg PE/hour. The MFR<sub>2</sub> and density of the PE product were estimated to be about 10 g/10 min and 970 kg/m<sup>3</sup> respectively. The slurry was withdrawn continuously and introduced into a second loop reactor of volume 500 dm<sup>3</sup>, operating at 95°C and 61 bar. Additional ethylene, propane and hydrogen were added to produce a PE of MFR<sub>2</sub> 330 g/10 min and density 974 kg/m<sup>3</sup> at 30 kg PE/hour. The polymer, which contained the active catalyst, was continuously withdrawn, separated from the reaction medium and transferred to a gas phase reactor. Here

additional ethylene, hydrogen and 1-butene comonomer were added to produce a PE of  $MFR_{21}$  7.3 g/10 min and density 949 kg/m<sup>3</sup> at 69 kg PE/hour. The low MW (high MFR) fraction thus represented 45% of the total polymer.

### EXAMPLE 3

#### Bimodal HDPE Polymer Production

Polymerization was effected as in Example 2 except that 36 kg PE/hour was formed in the second loop reactor, 77 kg PE/hour was formed in the gas phase reactor and the  $MFR_{21}$  and density of the final PE were 3.3 g/10 min and 952 kg/m<sup>3</sup> respectively. The low MW (high MFR) fraction represented 48% of the total polymer.

### EXAMPLE 4

#### Bimodal HDPE Polymer Production

Ethylene, propane and hydrogen were introduced into a 50 dm<sup>3</sup> slurry loop reactor operating at 80°C and 65 bar at 2.0 kg/hour, 28 kg/hour and 1 g/hour respectively. A catalyst according to Example 3 of EP-B-688794 was added to produce PE at a rate of 1.6 kg PE/hour. The  $MFR_2$  and density of the PE were estimated to be about 10 g/10 min and 970 kg/m<sup>3</sup> respectively. The slurry was continuously withdrawn and introduced into a second loop reactor of 500 dm<sup>3</sup> volume operating at 95°C and 61 bar. Additional ethylene, propane and hydrogen were added so that the second loop reactor produced PE at a rate of 34 kg PE/hour with  $MFR_2$  and density of 55 g/10 min and 970 kg/m<sup>3</sup> respectively. PE polymer, containing the active catalyst, was withdrawn continuously from the second loop reactor, separated from the reaction medium and transferred to a gas phase reactor where additional ethylene, hydrogen and 1-butene comonomer were added

such that PE was produced at 70 kg PE/hour with  $MFR_{21}$  and density of 6.9 g/10 min and 948 kg/m<sup>3</sup> respectively. The fraction of low MW (high MFR) polymer was thus 50%.

#### EXAMPLE 5

##### Bimodal HDPE Polymer Production

Polymerization was effected as in Example 4 except that 38 kg PE/hour and 78 kg PE/hour were formed in the second loop reactor and the gas phase reactor respectively. The final PE had  $MFR_{21}$  and density of 7.3 g/10 min and 948 kg/m<sup>3</sup> respectively and the low MW fraction was 50%.

#### EXAMPLE 6

##### Blow Moulding

30L containers were blow moulded on a Krupp Kautex KB50 blow moulding machine at an extruder temperature of 210°C using the HDPE polymers of Examples 2 to 5. The containers were pre-stored at 42°C for 3 weeks containing n-butyl acetate. The n-butyl acetate was replaced with ethylene glycol and the containers were cooled to -20°C within 24 hours and drop-tested at -20°C using the test method of ASTM 2463-90, giving values of 2 to 3.25 m. The ESCR  $F_{50}$  values were also determined using ASTM D1693, condition B.

#### EXAMPLE 7

##### Polymer Properties

The measured properties of the polymers of Examples 2 to 5 and a comparison PE prepared using a chromium based catalyst are set out in Table 1 below. The comparison

PE is commercially available as HE8214 from Borealis AS.

Property	Example 2	Example 3	Example 4	Example 5	HE 8214
MFR <sub>21</sub> (g/10 min)	7.3	3.3	6.9	7.3	2.7
Density (kg/m <sup>3</sup> ) *	948.5	951.5	947.9	948	950.4
Mw	260000	370000	305000	316000	345000
Mn	8300	7700	12000	16000	16000
MWD	31	48	25	20	22
Tensile Modulus (mPa) <sup>†</sup>	920	1030	920	910	1065
ESCR F50 (hours)	542	>1000	>1000	>1000	391
Comonomer	1-butene	1-butene	1-butene	1-butene	1-hexene
Comonomer content (% wt)	1.8	1.1	1.4	1.2	<0.1

\* ISO 1183

† ISO 527-2

Claims

1. A process for the preparation of an 2 to 250L volume polyethylene container which process comprises blow moulding a bimodal HDPE.
2. A process as claimed in claim 1 wherein said HDPE contains an ethylene homopolymer having a weight average molecular weight of 20000 to 40000 D.
3. A process as claimed in either of claims 1 and 2 wherein said HDPE has a density of 945 to 975 kg/m<sup>3</sup>.
4. A process as claimed in any one of claims 1 to 3 wherein said HDPE has a density of 945 to 960 kg/m<sup>3</sup>, a weight average molecular weight of 250000 to 350000 D, a number average molecular weight of 7000 to 18000 D, a molecular weight distribution of 18 to 50, an MFR<sub>21</sub> of 3 to 8 g/10 min, a tensile modulus of at least 900 mPa, and a comonomer content of 1 to 2 wt. %.
5. A blow-moulded bimodal HDPE container having a volume of 2 to 250L, and an ESCR F<sub>50</sub> of at least 500 hours.